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Vibrational features of water at the low-density/high-density liquid structural transformations

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ABSTRACT

A structural transformation in water upon compression was recently observed at the temperature $T = 277$ K in the vicinity of the pressure $p \approx 2\,000$ atm [R.M. Khusnutdinoff, A.V. Mokshin, J. Non-Cryst. Solids 357 (2011) 1677]. It was found that the transformations are related with the principal structural changes within the first two coordination shells as well as the deformation of the hydrogen-bond network. In this work, we study in detail the influence of these structural transformations on the vibrational molecular dynamics of water by means of molecular dynamics simulations on the basis of the model Amoeba potential ($T = 290$ K, $p = 1.0 \div 10\,000$ atm). The equation of state and the isothermal compressibility are found for the considered (p, T)-range. The vibrational density of states extracted for *THz*-frequency range manifests two distinct modes, where the high-frequency mode is independent of pressure whereas the low-frequency one has the strong, non-monotonic pressure-dependence and exhibits a step-like behavior at the pressure $p \approx 2000$ atm. The extended analysis of the local structural and vibrational properties discovers that there is a strong correlation between the primary structural and vibrational aspects of the liquid–liquid structural transformation related with the molecular rearrangement within the range of the second coordination shell.

1. Introduction

The physico-chemical features and soluble properties of water are of central importance for life on our planet. However, despite of a knowledge of some properties at the ambient conditions that corresponds only to the narrow part of the water phase diagram, the inherent structural and dynamical properties are still far from to be completely understood, that motivates to perform a large number of experimental and theoretical investigations of water [1–13]. Water is known as a 'system' with a rich variety of anomalous behavior related with different phase states. For example, in the solid state, water has at least fifteen crystalline forms, where four of these can coexist with the liquid phase, and a variety of amorphous phases known as amorphous ice and polyamorphism [2,14,15].

One of the interesting features of water, related with the first-order like phase transition from the low-density liquid (LDL) state to the high-density liquid (HDL) state, was reported in Ref. [16]. The hypothesis of a "liquid–liquid phase transition" in water was considered in a series of experimental, computational and theoretical studies (see, for example, Refs. [17–19] and references therein). As it was found, the difference between these liquid states is mainly provided by the structural properties. Namely, in the HDL, the local tetrahedrally coordinated hydrogen bond (HB) structure is not fully developed, whereas in the LDL, a more open, locally "ice-like" HB network is realized [1,3]. Both these liquid states are closely associated with the two amorphous phases observed experimentally in water: the low-density amorphous (LDA) and the high-density amorphous (HDA) ice, although locus of this "transition" is still debatable [15,18–20]. Remarkably, that

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